DIFFUSION BONDING OF ALUMINA TO STEEL USING COPPER INTERLAYER

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Presented here are the mechanical and microstructural properties of bonded joints of ceramics and steel with an elastic interlayer made of copper. The joints were executed by the direct bonding technique. Reaction layer was a mixture of oxides CuO and Cu_2O. The joints were bonded at temperature of 1348K (1075°C) in an atmosphere of nitrogen having oxygen content of about 10 ppm.
Tests of shear strength were carried out on ceramic-copper and steel-copper joints of different proportions of CuO and Cu_2O in the reaction layer. It was conduded that the mechanical strength of joints increases with the content of CuO in the metallizing paste. Ceramic-copper joints made with copper oxide have the strength of 80 MPa, those of steel-copper about 50 MPa. X-ray and microscopy examinations were carried out.
Hypothesis on the formation of diffusion joints ceramic-copper-steel through the synhwesis of spinels $CuAl_2O_4$ and $CuFe_2O_4$ was formulated.

INTRODUCTION

Experiments carried out confirm that multilayer bonding using thin and flexible interlayer solves the problem of making alumina - steel joints with of large dimensions. This type of interlayer reduces stresses generated during the bonding cycle. We are of the oppinion that the material most suitable for this purpose is copper because:

1. Copper is cheeper than other materials wich give ith similar results (Ag, Au, Pt),
2. Copper does not form brittle intermetalic compounds with iron.

Joining steel with alumina through a copper interlayer we obtained a bon-

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ding structure been shown in Fig.1.

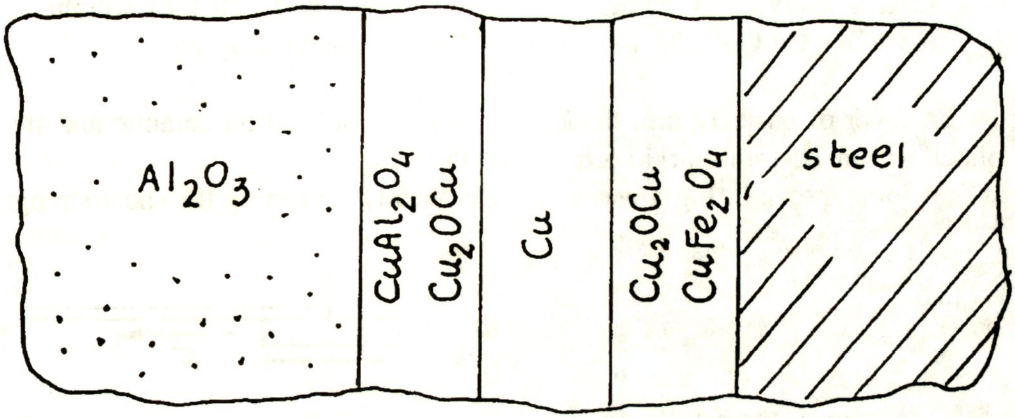

Fig.1 Scheme of an alumina-steel joint with copper interlayer.

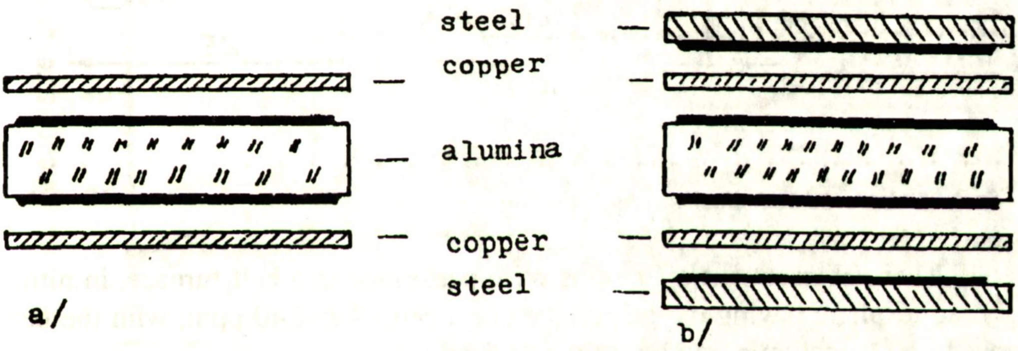

Fig.2 Sandwich packs designed for electron microscopy and X-ray diffraction investigations. Coats of oxides which had been made on the surfaces of ceramic and steel plates were obtained using screen printing technique.

For electron microscopy and X-ray diffraction sandwich packs 30x50 mm were prepared as shown in Fig.2. Thickness of individual plates: 1.5 mm for ceramics, 0.3 mm for copper foil and 1mm for steel.

Plates of alumina with 97.5% Al_2O_3 content were used in the experiments. Plate surfaces were coated, using the screen printing technique, with pastes prepared from the following powders:

1. CuO analytically pure,
2. CuO + Cu_2O - 50% by weight,
3. CuO + Cu_2O - 70% by weight
4. Cu_2O analytically pure.

A layer of paste 12 mm thick, after drying, was laid on ceramic and steel plates with a 1.5 mm margin left around.their edges.

A joint shown in Fig.3 was made specifically for testing the shear strength

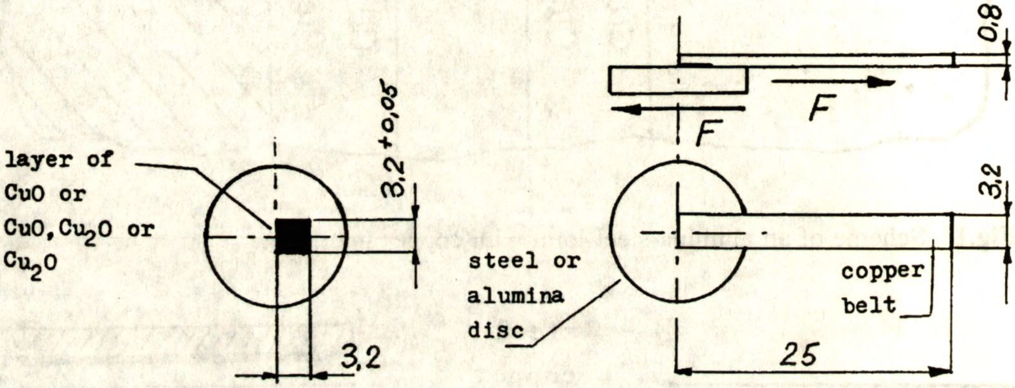

Fig.3 Joint used for shear strength testing.

Thermal treatment operations were performed in a belt furnace, in nitrogen atmosphere having oxygen content between 10 and 40 ppm, with the belt speed of 1.2 inch/min and hold time of 5 min.

Temperatures of tree furnace zones:

1.	1338 K,	1338K,	1333K	for sandwiched packs Fig.2.
		1065°C,	1065°C	1060°C
2.	1348 K,	1348 K,	1343 K	for joint shear strenght testing. Fig.3.
		1075°C,	1075°C,	1070°C

RESULTS

Mechanical strength.

Shear strength was measured with the use of Heckert testing machine. The setting of strain increase rate was 3 mm/min. The force was applied along the center line of the copper belt, parallel to the joint, at a distance of 5 mm from joint area.

The results of shear strength measurements have been plotted in Fig.4, as a function of the composition of the coat of oxides.

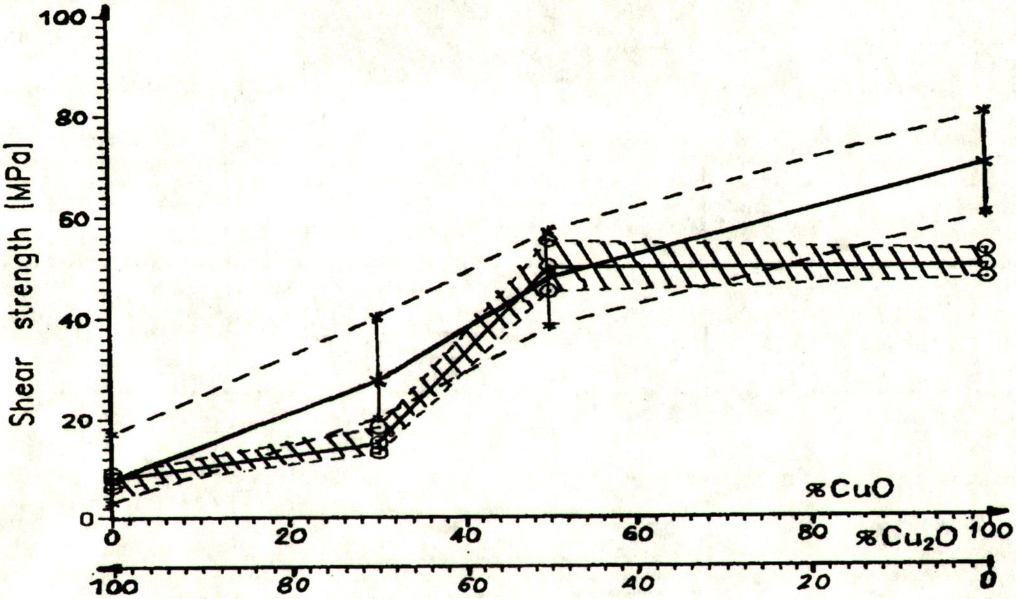

Fig. 4 Shear strength of the bonds: × - ceramics-copper, o - steel-copper.

The highest strength at 74 MPa was manifested by ceramic-copper joints bonded with a CuO coat, the lowest at 5MPa - by those bonded with a Cu_2O coat. A tenfold increase of the joint strength follows from the replacement of 50% Cu_2O by CuO. The location of joint failure in the strongest - CuO bonded joints-was in ceramics at a depth of 1 to 2 mm from the interface.

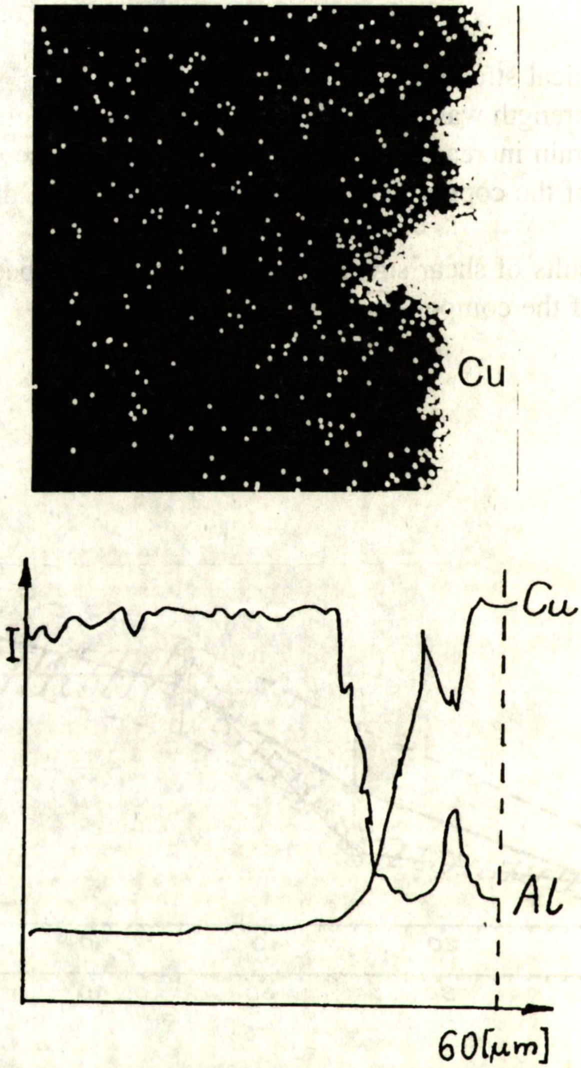

Fig.5 Distribution of Al and Cu in a Al_2O_3-Cu joint, bonded with a layer of CuO. Pattern of copper distribution at the boundary of phases.

Joint failure due to shear of steel-copper bonds occurs also inside steel. The strengths of the joints bonded with CuO and with a CuO, Cu_2O 50% mix are comparable: - amounting to ca. 55 MPa. As the content of Cu_2O in the coat increases, ensue a reduction of mechanical strength down to a few MPa.

Fig.6 Surface microstructure of copper torn aparat from alumina after bonding with CuO at 1348K (1075°C) SEM, x 2000.

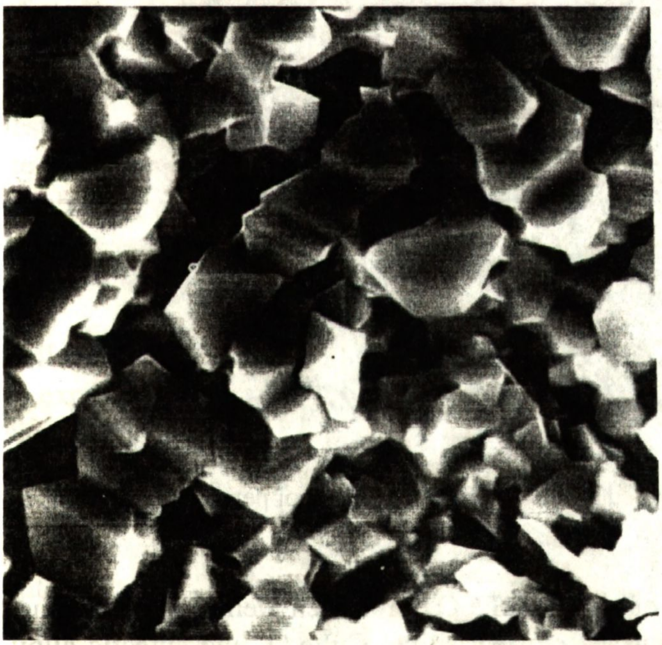

Fig.7 Surface microstructure of steel after tearing apart. Microstructure of the joint is shown in Fig.8.

The ceramics-copper joints were also subjected to X-ray and microscopy examination. The presence of aluminium-copper spinel was revealed on polished metallographic specimen of alumina-copper joints bonded with CuO layer with the use of electronic probe. Fig.5 presents linear distribution of Al and Cu in the joint. The zone of Al and Cu interpenetration is clearly visible both from the map of elements distribution and the linear concentration diagram.

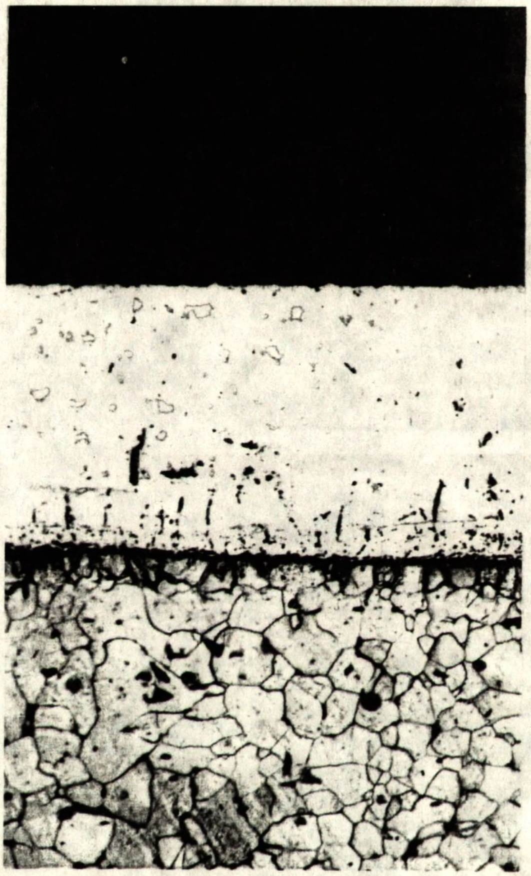

Fig.8 Microstructure of a bonded pack alumina ceramics-copper-steel. Metallographic microscop Neophot x 200.

Considerable amounts of spinel $CuFe_2O_4$ have been identified on the surface of copper, but on the surface of steel spinel $CuFe_2O_4$ and eutectic alloy Cu_2O Cu was found. By using the electronic probe it was possible to confirm the presence of Fe and Cu on both of the separated surfaces. Figs. 6 and 7 show the microstructure of the surfaces.

Large concentrations of crystalic products of bonding are visible on both the copper and steel surfaces: - crystals of spinel $CuFe_2O_4$.

Fig. 8 illustrates the microstructure of a bonded pack alumina-copper-steel where coat of 50% CuO/Cu_2O mix of oxides were put on alumina and steel. A significant penetration of liquid phase into steel is visible at grain boundaries, whereas no excessive amounts of phase Cu_2O Cu are observed in alumina-copper joint.

DISCUSSION

The investigations carried out prove that a high-strength joint of alumina-copper-steel may be produced by coating the alumina and steel with a CuO layer, at bonding temperature 1348K (1075°C), time of 5 min., and in the protective atmosphere of nitrogen containing 10 to 40 ppm of oxygen.

The shear strength of ceramics-copper joints is about 80 MPa, and that of steel-copper joints about 50 MPa, which is comparable with the strength of joints of this type made by other bonding technologies [1-3].

In order to reveal the phenomena accompanying bonding, a comparative testing has been conducted by replacing the cupric oxide CuO by cuprous oxide Cu_2O. The joints made using Cu_2O coats have a very low mechanical strength of about 5MPa,which is not suitable for practical application. The strength of bonds obtained using a mixture containing equal proportions of CuO and Cu_2O by weight appears to be ten times higher.

Microstructure examination using SEM and X-ray diffraction, made on polished sections and surfaces of joints torn apart, gave sufficient information to explain the process and to formulate a hypothesis of formation of the diffusion alumina-copper bonds.

In the high mechanical strength joints spinel $CuAl_2O_4$ has been identified, as well as an amorphous phase (Fig. 6) - probably Cu_2O-Cu eutectic.

Acoording to our investigations, the formation of a bonding layer as an eutectic Cu_2O-Cu is only possible if Cu_2O is present in active form e.g., as a product of decomposition of cupric oxide - above the temperature 643K (370 °C) - of thermodynamic equilibrium between CuO and Cu_2O.

A lower content of oxygen in nitrogen, not exceeding 40ppm, shifts the conditions of chemical equilibrium towards formation of Cu_2O as a product of CuO decomposition(in statu nascendi)

$$2\,CuO \longrightarrow Cu_2O + 1/2\,O_2 \qquad (1)$$

$$K = \frac{a_{Cu_2O} \times P_{O_2}^{0.5}}{a_{CuO}^2} \qquad 1$$

The newly generated active Cu_2O will react with Al_2O_3 to produce spinel $CuAl_2O_4$, the reaction being initiated in solid phase. Oxygen released in a closed space of reaction forms the Cu_2O oxide and Cu_2O Cu eutectic on the surface of copper , accelerating the mass transport during the growth of spinel phase. A strong diffusion bond is formed at the melting temperature of the eutectic (Fig. 8). A scheme of the course of reaction is shown in Fig.9.

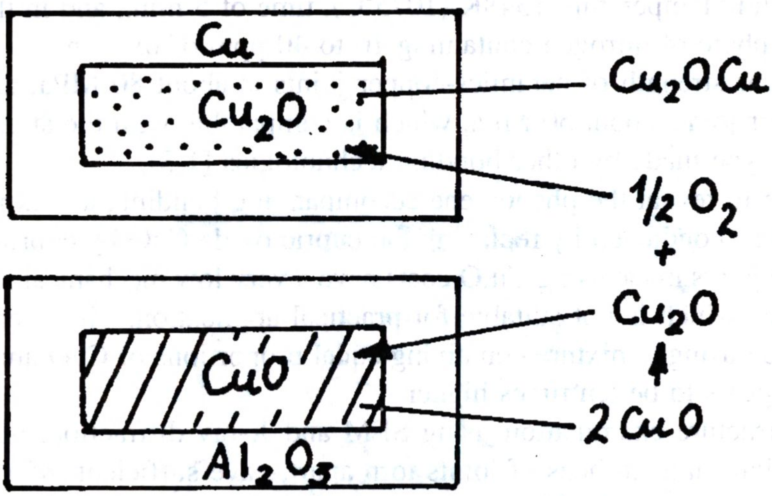

Fig.9 A scheme of formation of the alumina-steel joint with copper interlayer.

The same course of reaction occurs for alumina coated with CuO powder or with 50% (by weight) CuO+Cu_2O mix. In the latter case the quantity of the newly generated phases is much smaller. On ceramics coated with Cu_2O the occurence of sintered cuprous oxide Cu_2O and traces of Cu_2O Cu alloy.is observed.

In our investigations there was no evidence of the presence of spinel $CuAlO_2$, as identified in other works described in the literature [4,5]. The authors of paper [5] suggest the formation of spinel $CuAlO_2$ 1273K (1000°C) in a reaction

$$Cu_2O + Al_2O_3 \longrightarrow 2\ CuAlO_2 \qquad (2)$$

which is thermodynamically possible.

According to the authors of [4,5], formation of the second spinel $CuAl_2O_4$ requires conditions more oxidizing, and originates from the $CuAlO_2$ phase, to follow the reaction:

$$2\ CuAlO_2 + 1/4\ O_2 \longrightarrow CuAl_2O_4 + 1/2\ Cu_2O \qquad (3)$$

A detailed investigation of the generation of spinel has been conducted by the authors of paper [5]. They isolated and identified the spinel after 12 hours of soaking of the system:

Cu initially oxidized + Al_22O_3, at temperature 1343K (1075 °C), in nitrogen atmosphere.

According to the authors of [5], spinel $CuAlO_2$ crystallizes in a rhombohedral system, and is characterized by a highly anisotropic expansion coefficient. This property is, according to them, responsible for the low strength of the joints bonded by a layer containing spinel $CuAlO_2$.

The crystallographic structure of the both spinels is interpreted in different ways. According to [6], spinel $CuAlO_2$ has a hexagonal structure, while $CuAl_2O_4$ - a cubic one.

The present authors identified spinel $CuAl_2O_4$ in bonding with the use of CuO or CuO+ 50% Cu_2O; such joints display a high mechanical strength. Apart from spinel there were found considerable amount of amorphous phase (Fig.6) probably from a near-eutectic liquid. Only traces of the amorphous phase on ceramics were found in joints bonded using Cu_2O or a mix of CuO + 70% Cu_2O.

Mechanical strength of both the steel-copper joints with CuO coat and with CuO + 50% Cu_2O coat on steel was the same: around 50 MPa. In both cases it was found that the bond is primarily due to the contribution of the spinel phase, with only minor part of the amorphous phase.

After tearing apart of the steel-copper joint there was spinel $CuFe_2O_4$ identified on the copper and steel plates, while on the steel minor ammounts of the amorphous phase(possibly near-eutectic liquid). In the steel-copper joints, bonded under the same conditions as the alumina-copper joints the quantity of the spinel phase generated is many times larger (Fig. 7). The number of newly-generated phases may be reduced by restricting the quantity of CuO (O_2) at the interface during bonding. In other experiments the authors identified only FeO during bonding of Armco iron-ETP to copper containing 0.04% O_2 [7].

The mechanical strength of alumina-copper joints, analogously to the strength of steel-copper joints is high, only when if a new spinel phase would be generated in the intermediate layer. A scheme of formation of the alumina-steel joint with copper interlayer has been presented in Fig.1.

To summarize: a decisive part in the bond formation belongs to oxygen and cuprous oxide in situ, released in the reaction of CuO reduction, as well as to the new oxides Cu_2O and FeO, generated from reactions of active O with copper and steel. Due to the high plasticity of copper and its close adhesion to the surfaces of alumina and steel at high temperatures, the transport of oxygen to the interface of phases is of great importance. The contribution of atmospheric oxygen in the bonding process is nil, as its content is only 10 to 40 ppm. It is, therefore, important to secure a source of supply of oxygen to the interface of bonding, e.g. by development of the surface of alumina, by using copper with large oxygen content or by utilization layers of oxides on the surfaces of copper or ceramics. Then the conditions favouring the formation of intermediate phase-spinel $CuAl_2O_4$.

CONCLUSIONS

1. Good strenght joins of alumina-copper and alumina-steel with copper interlayer were obtained by liquid bonding with Cu_2OCu where CuO was a source of active Cu_2O and oxygen which, at the next stage, produced spinel layer $CuAl_2O_4$ and $CuFe_2O_4$.
2. In comparison with previous works there is a decrease in of intergrain corrosion of copper using a layer of CuO+Cu_2O.
   Probably at the some time
   $2CuO \rightarrow Cu_2O + 1/2O_2$
   and a Cu is obtained as a product of reduction
   $Cu_2O \rightarrow 2Cu + 1/2O_2$
   which gives us liquid eutectic melt Cu_2OCu
3. Mechanical strength of the alumina-copper and steel-copper joints increases with thequantity of active Cu_2O generated also the amount of spinels $CuAl_2O_4$ and $CuFe_2O_4$ increases.

REFERENCES

[1] Włosiński W., Olesińska W.: Influence of Ti on active role and penetration of AgCuTiSn solder components into alumina. Submitted to III ECERS Conf., Madrid 1993

[2] Shalz M.L.,Dalgleish B.J.,Tomosia A.P.,Glaeser A.M.: Ceramic joining, J.of Matl.Sci. 1993, 28, 1673-1684

[3] Electronic Production,Vol.3, 5,1974, 32

[4] Urena A., Gomez de Salazar J.M., Quinones J.: Diffusion bonding of alumina to steel using soft copper interlayer, J.of Matl. Sci. 27,1992, 599-606

[5] Sung Tae Kim, Chong Hee Kim: Interfacial reaction product and its effect on the strength of copper to alumina eutectic bonding, J.of Matl. Sci.27, 1992, 20612066

[6] Beraud C., Courbiere M., Esnouf C., Juve D., Treheux D.: Study of copper-alumina bonding, J.of Matl.Sci.24, 1989, 4545-4554

[7] Calvo F.A., Urena A., Gomez de Salazar J.M., Molleda F.: Tensile strength of Armco iron-ETP copper diffusion bonds J.of Matl. Sci. Letters 8, 1989, 137140